

Supplementary Information

Electric field dependent photocurrent generation in a thin-film organic photovoltaic device with a [70]fullerene-benzodifuranone dyad†

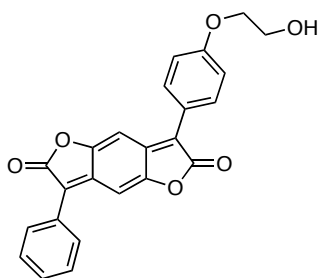
Pirmin A. Ulmann,^a Hideyuki Tanaka,^a Yutaka Matsuo,^{*a} Zuo Xiao,^a Iwao Soga,^b and Eiichi Nakamura^{*a}

^a Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. Fax: +81-3-5841-4356; Tel: +81-3-5800-6889; E-mail: matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

^b Mitsubishi Chemical Group Science and Technology Research Center, Inc., Yokohama 227-8502, Japan

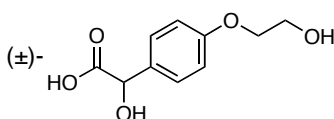
1.	Synthetic procedures	S2
2.	Dynamic Scanning Calorimetry (DSC) trace for compound 3	S5
3.	Cyclic voltammogram of compound S3	S5
4.	UV/Vis and photoluminescence spectrum of compound S3	S6
5.	Simulation of IPCE spectra	S6
6.	Calculated IPCE spectra of the pn heterojunction devices	S7
7.	References	S7

1. Synthetic procedures



3-(4-(2-Hydroxyethoxy)phenyl)-7-phenylbenzo[1,2-*b*:4,5-*b'*]difuran-2,6-dione (**2**)

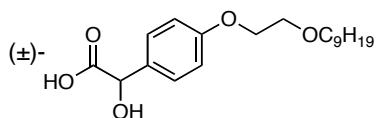
[1]: Compound **S1** (267 mg, 1.26 mmol) and 5-hydroxy-3-phenylbenzofuran-2(3*H*)-one [2] (420 mg, 1.86 mmol, 1.48 equiv) were mixed together and heated to 195 °C over the course of 45 min while stirring. The viscous red oil was stirred for another 1.5 h at 195 °C. Column chromatography (EtOAc/CH₂Cl₂ 1:9) afforded a red band that was concentrated *in vacuo*. The intermediate product was dissolved in THF (10 mL) and chloranil (227 mg, 0.923 mmol, 0.73 equiv) was added, followed by stirring at 65 °C for 2 h, resulting in a darkened red solution. Column chromatography (EtOAc/CH₂Cl₂ 1:10 to 1:3) afforded **2** as a dark red powder (186 mg, 0.465 mmol, 37% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.6 (br s, 1H, OH), 4.03 (t, *J* = 4.0 Hz, 2H, CH₂OH), 4.18 (t, *J* = 4.0 Hz, 2H, CH₂OAr), 6.90 (s, 1H, benzodifuranone), 6.92 (s, 1H, benzodifuranone), 7.08 (d, *J* = 8.6 Hz, 2H, Ar), 7.47-7.55 (m, 3H, Ar), 7.79-7.84 (m, 4H, Ar); ¹³C NMR spectra could not be obtained because of low solubility; UV/Vis (CH₂Cl₂): λ_{max} [nm] (ε [L mol⁻¹ cm⁻¹]) = 326 (6'000), 497 (41'000); APCI-HRMS (-): calcd for C₂₄H₁₆O₆ [M⁻] 400.0947, found 400.0955.



(±)-2-Hydroxy-2-(4-(2-hydroxyethoxy)phenyl)acetic acid (**S1**) [3]: (±)-4-

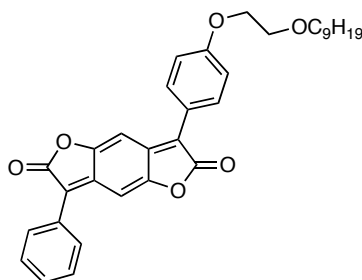
Hydroxymandelic acid (1.50 g, 8.92 mmol) was dissolved in water, followed by the addition

of 2-chloroethanol (2.3 mL, 34 mmol, 3.8 equiv). The mixture was heated to 90 °C. Aqueous NaOH (1.9 M, 15 mL, 29 mmol, 3.3 equiv) was added dropwise into the reaction mixture over 50 min and the solution was then kept stirring at 90 °C for 15 h. The flask was put into an ice bath and aqueous hydrochloric acid (37%, 1.5 mL) was added slowly, which resulted in the formation of a white precipitate. Filtration and recrystallization from water (ca. 20 mL) afforded **S1** as a white powder (991 mg, 4.67 mmol, 52% yield). ^1H NMR (500 MHz, d_6 -DMSO) δ 3.69 (q, $J = 4.6$ Hz, 2H, CH_2OH), 3.95 (t, $J = 4.6$ Hz, 2H, CH_2OAr), 4.85 (t, $J = 5.0$ Hz, 1H, CH_2OH), 4.94 (s, 1H, CHCO_2H), 5.75 (br s, 1H, CHOH), 6.89 (d, $J = 9.2$ Hz, 2H, Ar), 7.29 (d, $J = 9.2$ Hz, 2H, Ar), 12.5 (br s, 1H, CO_2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, d_6 -DMSO) δ 59.52 (1C, CH_2OH), 69.45 (1C, CH_2OAr), 71.86 (1C, CH), 114.04 (2C, Ar), 127.83 (2C, Ar), 132.22 (1C, Ar), 158.17 (1C, Ar), 174.29 (1C, CO_2H); APCI-HRMS (-): calcd for $\text{C}_{10}\text{H}_{11}\text{O}_5$ [$\text{M} - \text{H}$] $^-$ 211.0607, found 211.0591.



(±)-2-Hydroxy-2-(4-(2-(nonyloxy)ethoxy)phenyl)acetic acid (S2): Compound **S1** (300 mg, 1.41 mmol) was dissolved in DMSO. 1-Bromononane (400 μL , 2.09 mmol, 1.5 equiv) and $\text{N}(n\text{-butyl})_4\text{HSO}_4$ (24 mg, 0.071 mmol, 0.05 equiv) were added and the reaction mixture was stirred vigorously at 24 °C. NaOH (284 mg, 7.1 mmol, 5 equiv) was dissolved in water (300 μL) and was added dropwise to the reaction mixture over 20 min. The reaction mixture was then heated to 45 °C and stirred for 18 h, resulting in a slightly yellow suspension. Addition of aqueous hydrochloric acid (ca. 0.5 M, 20 mL), followed by stirring for 2 h resulted in the formation of a precipitate that was filtered and washed with water (5 mL) and hexane (10 mL). Recrystallization from EtOH afforded **S2** (106 mg, 0.313 mmol, 22% yield) as a white powder. ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H, CH_3),

1.23-1.30 (m, 12H, CH₂), 1.58-1.62 (m, 2H, OCH₂CH₂), 3.53 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.79 (t, *J* = 4.6 Hz, 2H, ArOCH₂CH₂O), 4.11 (t, *J* = 4.6 Hz, 2H, ArOCH₂), 5.18 (s, 1H, CHOH), 6.89 (d, *J* = 8.6 Hz, 2H, Ar), 7.33 (d, *J* = 9.2 Hz, 2H, Ar); ¹³C{¹H} NMR (125 MHz, *d*₆-DMSO) δ 13.91 (1C, CH₃), 22.04 (1C, CH₂), 25.57 (1C, CH₂), 28.60 (1C, CH₂), 28.80 (1C, CH₂), 28.94 (1C, CH₂), 29.11 (1C, CH₂), 31.23 (1C, CH₂), 67.12 (1C, CH₂O), 68.49 (1C, CH₂O), 70.35 (1C, CH₂O), 71.82 (1C, CH), 114.04 (2C, Ar), 127.83 (2C, Ar), 132.31 (1C, Ar), 157.99 (1C, Ar), 174.28 (1C, CO₂H); APCI-HRMS (-): calcd for C₁₉H₂₉O₅ [(M - H)⁻] 337.2015, found 337.2008.

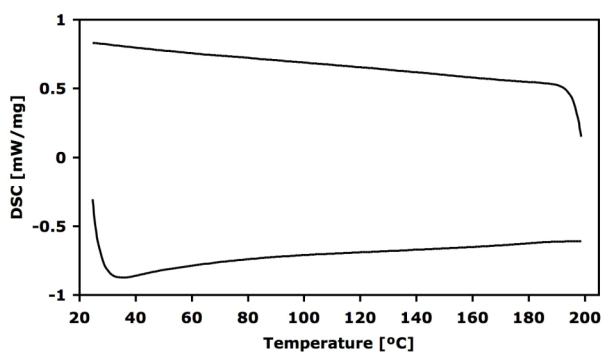


3-(4-(2-(Nonyloxy)ethoxy)phenyl)-7-phenylbenzo[1,2-*b*:4,5-*b'*]difuran-2,6-dione

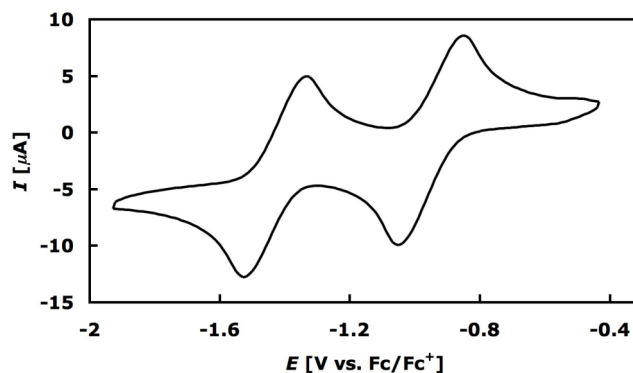
(S3): Compound **S2** (89 mg, 0.26 mmol) and 5-hydroxy-3-phenylbenzofuran-2(3*H*)-one [2] (85 mg, 0.38 mmol, 1.5 equiv) were mixed together and heated to 195 °C over the course of 45 min while stirring. The viscous red oil was stirred for another 2.5 h at 195 °C. Column chromatography (CH₂Cl₂) afforded a red band that was concentrated *in vacuo*. The intermediate product was dissolved in THF (5 mL) and chloranil (19 mg, 0.077 mmol, 0.30 equiv) was added, followed by stirring at 65 °C for 1 h, resulting in a darkened red solution. Column chromatography (CH₂Cl₂) afforded **S3** as a dark red powder (39.4 mg, 0.0673 mmol, 26% yield, ca. 90% purity). Further column chromatography (Hexane/CH₂Cl₂ 1:4) afforded analytically pure material (17.5 mg, 0.0332 mmol, 13% yield). ¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 6.9 Hz, 3H, CH₃), 1.26-1.34 (m, 12H, CH₂), 1.59-1.65 (m, 2H, OCH₂CH₂), 3.55 (t, *J* = 6.9 Hz, 2H, OCH₂), 3.82 (t, *J* = 5.2 Hz, 2H, ArOCH₂CH₂O), 4.21 (t, *J* = 4.6 Hz, 2H,

ArOCH₂), 6.89 (s, 1H, benzodifuranone), 6.92 (s, 1H, benzodifuranone), 7.08 (d, $J = 8.6$ Hz, 2H, Ar), 7.47-7.55 (m, 3H, Ar), 7.79-7.83 (m, 4H, Ar); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 14.09 (1C, CH₂), 22.66 (1C, CH₂), 26.07 (1C, CH₂), 29.26 (1C, CH₂), 29.46 (1C, CH₂), 29.56 (1C, CH₂), 29.62 (1C, CH₂), 31.87 (1C, CH₂), 67.74 (1C, OCH₂), 68.92 (1C, OCH₂), 71.81 (1C, OCH₂), 97.87, 98.49, 115.57, 122.35, 124.94, 125.73, 129.12, 129.19, 129.58, 130.33, 130.92, 136.27, 153.88, 154.53, 161.04, 167.80 (1C, C=O), 167.88 (1C, C=O); UV/Vis (CH₂Cl₂): λ_{max} [nm] (ϵ [L mol⁻¹ cm⁻¹]) = 331 (6'700), 501 (45'000); Φ_{Fl} (25 °C, CH₂Cl₂, standard: fluorescein in 0.1 M aq. NaOH, $\Phi_{\text{Fl}} = 0.93$ [4], corrected for refractive index) = 0.09; APCI-HRMS (-): calcd for C₃₃H₃₄O₆ [M⁻] 526.2356, found 526.2334.

2. Dynamic Scanning Calorimetry (DSC) trace for compound 3 (bottom: 1st heating, top: 1st cooling).

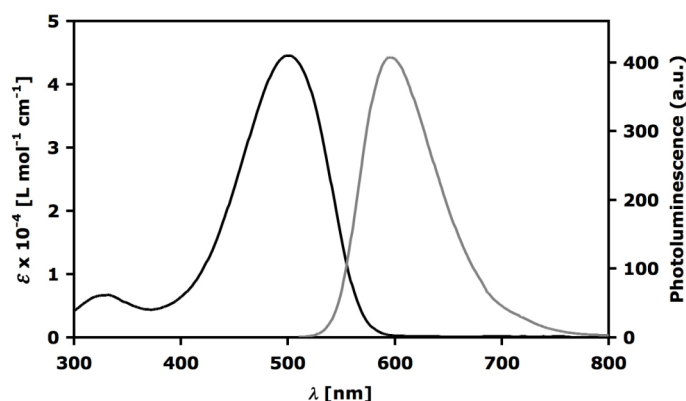


3. Cyclic voltammogram of compound S3 in THF.



$$E_{1/2}^{\text{red1}} = -0.95, E_{1/2}^{\text{red2}} = -1.43 \text{ V vs. Fc/Fc}^+$$

4. **UV/Vis and photoluminescence spectrum of compound S3 (in CH₂Cl₂, black: absorption, grey: photoluminescence, $\lambda_{\text{ex}} = 500$ nm).**



5. **Simulation of IPCE spectra**

IPCE spectra are explained based on the estimation of the number of photons absorbed in both donor and acceptor layer.[5] For simplicity, we assume an effective active thickness of the donor and acceptor layer (expressed as d_D^* and d_A^*), where all the absorbed photons are converted to electric current with internal quantum efficiencies of 75% and 99% for the donor and acceptor layer, respectively (Φ_D and Φ_A). These internal quantum efficiencies are roughly estimated from experimental results. The total number of electrons generated in the donor and acceptor are expressed by equation (1) and (2), respectively.

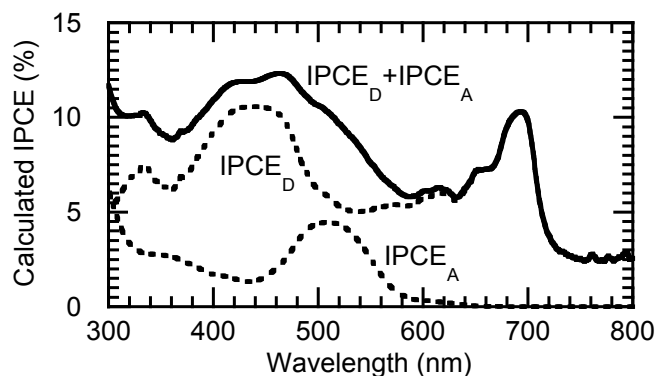
$$IPCE_D(\lambda) = \Phi_D \left(1 - e^{-\alpha_D(\lambda) \cdot d_D^*}\right) \left\{ e^{-\alpha_D(\lambda) \cdot (d_D - d_D^*)} + R_{Al} \cdot e^{[-\alpha_D(\lambda) \cdot d_D - 2 \cdot \alpha_A \cdot d_A^*]} \right\} \quad (1)$$

$$IPCE_A(\lambda) = \Phi_A \left(1 - e^{-\alpha_A(\lambda) \cdot d_A^*}\right) \cdot e^{-\alpha_D(\lambda) \cdot d_D} \cdot \left(1 + R_{Al} \cdot e^{-\alpha_A(\lambda) \cdot d_A^*}\right) \quad (2)$$

We assume reflectivity of the top aluminum electrode ($R_{Al} \approx 80\%$), transmittance of ITO, PEDOT:PSS, and the cathode buffer layer ($T \approx 100\%$). The absorption coefficients of the donor and acceptor (α_D and α_A) obtained from experimental results are used in this simulation. Total thickness of the donor and acceptor layer is d_D and d_A . In the Figure below (section 6), the calculated $IPCE_D$ and $IPCE_A$ spectra, assuming d_D^* and d_A^* to be 7 nm, are shown. Even

though we used quite rough assumptions for the calculation, the total IPCE spectra reproduce the features of the observed IPCE spectra well.

6. Calculated IPCE spectra of the pn heterojunction devices



7. References

- [1] a) R. D. McClelland, B. Parton, Condensation Polymers. *Eur. Pat. Appl.* 333337, 1989; b) N. Hall, R. W. Kenyon, Polycyclic Dyes. *Eur. Pat. Appl.* 1195412, 2002.
- [2] G. Hallas, C. Yoon, *Dyes Pigm.*, 2001, **48**, 107-119.
- [3] a) R. W. Kenyon, D. Thorp, Hetero-polycyclic Aromatic Compound. *Eur. Pat. Appl.* 146269, 1985; b) P. Nesvadba, 3-(2-Acyloxyethoxyphenyl)benzofuran-2-ones as Stabilizers. *Eur. Pat. Appl.* 591102, 1994.
- [4] R. Sjöback, J. Nygren, M. Kubista, *Spectrochim. Acta*, 1995, **Part A 51**, L7-L21.
- [5] A. K. Gosh, D. L. Morel, T. Feng, R. F. Shaw, C. R. Rowe, *J. Appl. Phys.*, 1974, **45**, 230-236.